

d- and f-orbital correlations in the REFeAsO compoundsT. MIYAKE^{1,4} *, L. POUROVSKII² †, V. VILDOSOLA^{2,3,4}, S. BIERMANN^{1,3}, A. GEORGES^{2,4}¹ *Research Institute for Computational Sciences, AIST, Tsukuba 305-8568, Japan*² *Centre de Physique Théorique, École Polytechnique, CNRS, 91128 Palaiseau, France*³ *Departamento de Física, Comisión Nacional de Energía Atómica (CNEA-CONICET), San Martín, Provincia de Buenos Aires, Argentina*⁴ *Japan Science and Technology Agency, CREST*

We estimate theoretically the strength of the local Coulomb interaction for the Fe 3*d* and Ce 4*f* shells in the REFeAsO compounds. In LaFeAsO and CeFeAsO we obtain values of the local Coulomb interaction parameter U for both Fe and Ce which are larger than those of elemental Fe and Ce metals. The Fe 3*d* bandwidth of REFeAsO is found to increase slightly as one moves along the RE-series. Using a combined local density approximation and dynamical mean-field theory (LDA+DMFT) approach, we study the behaviour of the localized 4*f* states along the rare-earth oxyarsenides REFeAsO series (RE=Ce,Pr,Nd). In CeFeAsO the occupied Ce 4*f* band is located just below the Fe 3*d* band leading possibly to a Kondo screening of the 4*f* local moment under applied pressure, while the unscreened local moment behaviour is expected for the Pr and Nd compounds.

KEYWORDS: high- T_c superconductors, Fe-oxipnictides, heavy-fermions**1. Introduction**

The discovery of high- T_c superconductivity in FeAs-based materials¹⁾ – the first non cuprates high- T_c superconductors – has triggered intensive research lately. As in the cuprates, the superconducting state (SC) occurs close to a long range SDW AF-type order²⁾ and is believed to originate from the quasi 2D FeAs layers, in which Fe forms a square lattice. Both the FeAs-based superconductors^{3,4)} and the cuprates⁵⁾ display a strong sensitivity of T_c on the relative atomic positions within the transition metal layer. In view of these similarities and of the well-known strongly correlated nature of the Cu-*d* band in the high- T_c cuprates, the strength of local Coulomb correlations in the FeAs superconductors is a key issue to be clarified. On the one hand, LDA can, apart from some shifts, account for the photoemission spectra qualitatively well.^{6,7)} Several works based on X-ray absorption experiments are also pointing to a weakly correlated behavior of these compounds⁸⁾ while a feature due to Fe 3*d* states localization, the lower Hubbard band, which is predicted by dynamical mean field theory (DMFT)⁹⁾ in the intermediate to strong correlation regime, has not yet been seen in

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spectroscopic experiments. On the other hand, it has been established that LDA calculations overestimate the strength of the Fe-As bonding leading to a substantial underestimation of the Fe-As bond length, this disagreement being only partially improved by GGA.¹⁰⁾ However, somewhat confusingly, LDA calculations (and not GGA) within optimized structures can account for the magnetic properties.^{10,11)} Some experimental facts also point to strong correlations, such as the bad metallicity (high resistivity) of the normal state,^{1,12)} the absence of a Drude peak in the optical conductivity¹²⁾ and strong temperature-driven spectral weight transfers in optical measurements.¹³⁾

Hence, whether the Fe 3*d* states in the oxypnictides are weakly or rather strongly correlated remains a largely open question. Another important issue is whether the localized RE 4*f* states play any significant role in the electronic properties of these materials, e.g. by hybridizing with the Fe 3*d* states and whether these RE states affect the superconducting properties of the REFeAsO compounds.

In this paper we study the evolution of the Fe 3*d* bandwidth and estimate theoretically the strength of the local Coulomb interaction for both the Fe 3*d* and RE 4*f* states, within the constrained RPA and LDA methods, respectively. We also study the evolution of the RE 4*f* band along the REFeAsO series (RE=Ce,Pr,Nd) using an approach that combines the local density approximation and dynamical mean-field theory (LDA+DMFT).

2. Band structure trends

The evolution of T_c along the series of rare earth elements, and possible correlations with structural properties have attracted particular interest. While LaFeAsO_{1-x}F_x has a T_c of 26 K, the critical temperature is drastically increased by replacing La by other rare earth ions (RE=Ce,Pr,Sm,Nd,Gd), up to ~ 55 K for Sm. Possible correlations between the evolution of T_c with changes in the structural parameters due to decreasing size of the rare-earth ions along the series have been reported in the literature.^{4,14)} Fig. 1 shows the evolution of the Fe-bandwidth from La to Sm calculated using the Full-Potential APW+local orbitals method as implemented in the Wien2k¹⁵⁾ code: the increase of the bandwidth is due to the decrease of the Fe-Fe distance and to the corresponding decrease of the Fe-As bond angle θ_3 . The most natural candidate to search for strong d-electron correlations thus appears to be the first member of the series, LaFeAsO, which has the smallest bandwidth.

3. d-orbital correlations

We have calculated the Coulomb interactions within the constrained RPA method proposed in Ref.¹⁶⁾ Within the random phase approximation (RPA), the polarisation P of a solid is calculated as a sum over all possible transitions between empty and occupied states, weighted by their respective energy differences. Whereas the fully screened Coulomb interaction is then calculated by screening the bare Coulomb interaction v by P , the onsite Hubbard

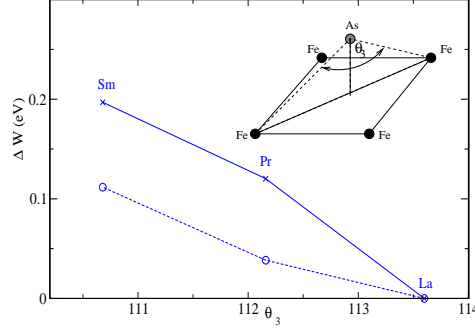


Fig. 1. The change ΔW in the Fe 3d full bandwidth W (solid line) and the bandwidth of its occupied part W_{occ} (dashed line) for several RFeAsO materials given with respect to θ_3 . The change ΔW is referenced to calculated value for LaFeAsO at its experimental structure²⁾ (4.25 eV for W and 1.95 eV for W_{occ}). The structural data for Pr and Sm compounds were taken from Ref.²⁰⁾ and,²¹⁾ respectively. *Inset*: Schematic Fe_4As pyramid for LaFeAsO in which θ_3 angle is indicated.

interaction is screened by a partial polarisation function that excludes all those screening processes that are included in the many-body model:

$$U = \frac{v}{1 - P_r v} \quad (1)$$

For a model retaining only d-bands, for example, $P_r = P - P_d$, where P_d is the polarisation function corresponding to d-d transitions only.

Obviously, matrix elements of the local interaction depend on which states are included in the model (and are thus not allowed to screen U) and - in a more trivial fashion - on the spread of the Wannier functions used for taking the matrix elements. We have calculated matrix elements of U and W in maximally localised Wannier basis, corresponding to different models: (i) The first one is a “d-only model”, where only d-d transition were cut out, and the Wannier construction was performed for the manifold of d-states only. (ii) The second choice is a “dpp-model”, where the whole block of Fe-d, As-p and O-p bands was used for the Wannier construction and for the truncation of the polarisation. (iii) The third option is a hybrid between the first two, in the sense that only the d-d transitions were cut out in the polarisation, but the Wannier functions from the dpp-model were used. When performing many-body calculations with a hamiltonian containing all dpp-states but including only U for the d-states, this last procedure should be the most appropriate way of evaluating the proper value of U to be used in such a framework.

As expected, the Hubbard interaction is smallest for the d-only model, where most of the screening has already been taken into account before the many-body treatment, and the Wannier orbitals are very extended.¹⁷⁾ The comparison between the dpp and d-dpp models allows to identify the contributions from the two effects: the screening processes taken into account are the same as in the d-model, but the orbitals are those of the dpp-model.

	v	U	J
d	15.99	2.92	0.43
dpp	20.31	4.83	0.61
$d-dpp$	20.31	3.69	0.58

Table I. Bare and partially screened Coulomb interactions v and U (orbitally averaged), as well as the Hund's coupling for LaFeAsO in the different Wannier constructions described in the text.

In absolute values, our results are somewhat bigger than the ones obtained in Ref.^{18,19)} and indicate that within a d - dpp model U values beyond 4 eV are not unrealistic. According to⁹⁾ this would place LaFeAsO close to the Mott transition. As discussed above, experimental photoemission spectra may not support this view. It is possible that effects not included in the single-site DMFT calculations (non-local Coulomb interactions mediated e.g. by the strong Fe-As hybridization, non-local self-energy effects, ...) are important to settle this issue.

4. f -orbital correlations

In order to study the evolution of the strongly localized $4f$ states along the rare-earth oxyarsenides REFeAsO series (RE=Ce,Pr,Nd) and their interaction with other bands, we have performed *ab initio* calculations using the combined local density approximation and dynamical mean-field theory (LDA+DMFT) approach, in the fully-selfconsistent framework described in.²³⁾ The local self-energy of the $4f$ shell has been computed by employing the atomic (Hubbard-I) approximation.²⁴⁾ This approach to local correlations has been shown to be appropriate for the localized $4f$ shells of rare-earths compounds.²³⁾ We have taken values of the Slater integrals F^2 , F^4 , and F^6 for the local Coulomb interaction from the optical measurements of.²⁵⁾ In order to determine the value of the local Coulomb interaction U on the $4f$ shell, we have performed constrained LDA calculations for CeFeAsO. and obtained a value of about 9.7 eV for U on the Ce $4f$ shell. This is substantially larger than the usual range of U values for pure Ce. This can be explained by the quasi two-dimensional environment of the rare-earth sites in the case of oxypnictides, resulting in a rather poor screening of the local Coulomb interaction.

In Fig. 2 we show the calculated LDA+DMFT band structure and partial densities of states for REFeAsO (RE=Ce,Pr,Nd). For the sake of comparison the LDA bands computed with the RE $4f$ treated as core are also shown (in blue color) in Fig. 2. The occupied $4f$ states are located in the range of energies from -4 to -5 eV in PrOFeAs, and below -6 eV for NdOFeAs. The occupied $4f$ states hybridize rather strongly with the oxygen p states, which are located mainly at the top of the As $4p$ /O $2p$ band. This $4f$ - $2p$ hybridization leads to some modifications at the top of the O/As p band in comparison with the f -in-core band structure. In contrast, the Fe $3d$ bands are not modified by the interaction with the $4f$ states, as one

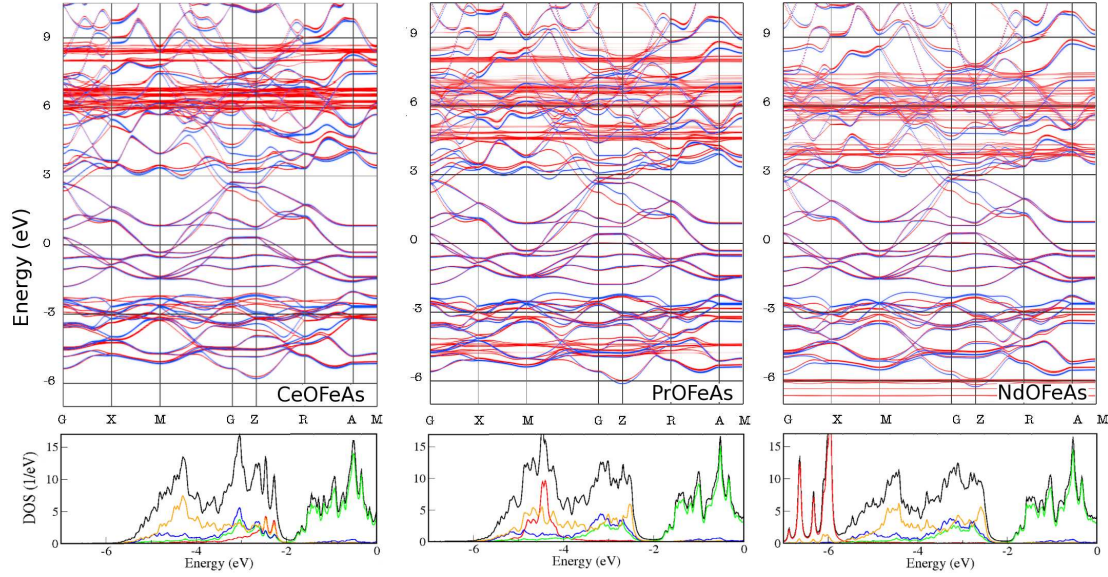


Fig. 2. Densities of states obtained within LDA+DMFT for REFeAsO (RE=Ce, Pr, Nd): total, partial RE 4*f*, Fe 3*d*, As 4*p* and O 2*p* shown by black, red, green, blue, and orange curves, respectively

may see in the upper panel of Fig. 2 where blue and red bands corresponding to Fe (close to the Fermi level) essentially coincide. The Pr and Nd 4*f* bands are located well below the Fe 3*d* bands. This implies that the Pr and Nd 4*f* shell simply leads to local moment behaviour, quite decoupled from other electronic states.

In contrast, in the Ce compound the occupied 4*f* band is located in the range of energies -2.2 to 3 eV, with the highest peaks of the 4*f* partial DOS at -2.3 and -2.5 eV. In experimental photoemission measurements of CeFeAsF_xO_{1-x}²⁶⁾ a peak at -1.7 eV has been assigned to the occupied Ce 4*f* band. Hence, the Ce 4*f* occupied states are located just below the Fe 3*d* bands. Therefore, in analogy to the case of CeFePO²⁷⁾ where the Kondo screening of the Ce 4*f* local moment was observed experimentally,²⁸⁾ one may expect Kondo screening of the 4*f* local moment by conduction electrons in CeFeAsO, particularly under applied pressure. In Ref.²⁷⁾ the corresponding Kondo temperature T_K has been estimated and its evolution under applied pressure investigated. The predicted rapid increase of T_K as function of pressure points to a possible competition between superconducting and heavy-fermion phases in CeFeAsO. This competition may be at origin of the rather rapid suppression of superconductivity observed in the doped CeFeAsO under pressure.

5. Conclusion

We have estimated the strength of the local Coulomb interaction U in the Fe 3*d* and RE 4*f* shells of the REFeAsO compounds. For both the 3*d* and Ce 4*f* states the U values in REFeAsO are substantially larger than the corresponding values for elemental Fe and Ce

metals. This can be explained by the layered structure of these materials resulting in less effective screening of the local Coulomb interactions. The obtained value of U for the Fe $3d$ shell is equal to 3.69 eV, which is rather close to the value of U used in recent LDA+DMFT calculations.⁹⁾ The value of U for the Ce $4f$ shell obtained by constrained LDA calculations for CeFeAsO is above 9 eV. We investigated correlation effects on the Re $4f$ shell of the REFeAsO compounds (RE=Ce,Pr,Nd) using the LDA+DMFT approach in conjunction with an atomic approximation. In the Pr and Nd compound the occupied $4f$ band is located well below the Fe $3d$ bands, implying unscreened local moment behaviour of the $4f$ states. In CeFeAsO the occupied $4f$ band is located just below the Fe $3d$ band, which may lead to Kondo screening under applied pressure and points to a competition between superconducting and heavy-fermion phases in this compound.

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